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Synthesis, supramolecular structure and thermal study of a new dinuclear zinc(II) complex derived from benzene-1,2,4,5-tetracarboxylic acid

Abstract: Reaction of benzene-1,2,4,5-tetracarboxylic acid (H_4L) with Zn(II) salt in DMF/MeOH leads to the formation of the new (μ_2 -benzene-1,2,4,5-tetracarboxylato-O,O')-hexaaqua-dizinc(II)-dihydrate complex $[Zn_2L(H_2O)_6] \cdot 2H_2O$ (**1**) (L = benzene-1,2,4,5-tetracarboxylate). Crystal structure analysis reveals that each tetracoordinated zinc(II) center adopts a distorted tetrahedral geometry occupied by one $O_{\text{carboxylate}}$ and three O_{water} atoms. A 3D supramolecular associate in the crystal lattice of **1** has been stabilized by a number of non-covalent interactions (O–H...O). Topology of the H-bonded 3D network has been also analyzed.

Keywords: benzene-1,2,4,5-tetracarboxylic acid; dinuclear zinc(II) complex; hydrogen bonding interaction; topological analysis.

DOI 10.1515/zkri-2014-1812

Received October 24, 2014; accepted December 9, 2014; published online January 21, 2015

Introduction

Studies on crystal engineering and supramolecular interactions have attracted much attention in recent years [1–3]. Aesthetic beauty, development of new topologies and utilization as functional materials of the supramolecular aggregates are the major aspects in this research area. Non-covalent interactions, namely, strong and weak hydrogen bonds, C–H... π interactions, π ... π stacking, halogen-halogen, sulfur-sulfur, gold-gold, etc. are being increasingly utilized to generate self-assembled structures [1–6].

On the other hand, varieties of bridging moieties [7–37] have been employed to synthesize dimeric to

polymeric complexes. Among them, carboxylates are the best, due to their versatile coordination behavior that generates multinuclear systems [9–37]. In fact, benzene carboxylates (di/tri/tetra/penta/hexa) are better choices to design dimer or multinuclear complexes. As for examples, a number of polymeric zinc(II) complexes derived from benzene-1,2,4,5-tetracarboxylic acid (H_4L) have been reported so far [15–28]. However, also few dimeric complexes containing this tetracarboxylic acid (H_4L) are reported [29–37] but not with zinc(II) ions. We anticipated that the reaction of zinc(II) salt with this carboxylic acid (H_4L) may also produce dinuclear complexes which can generate interesting supramolecular structures *via* non-covalent interactions. Thus to obtain a dinuclear zinc(II) complex from H_4L is one of the aim of the current study.

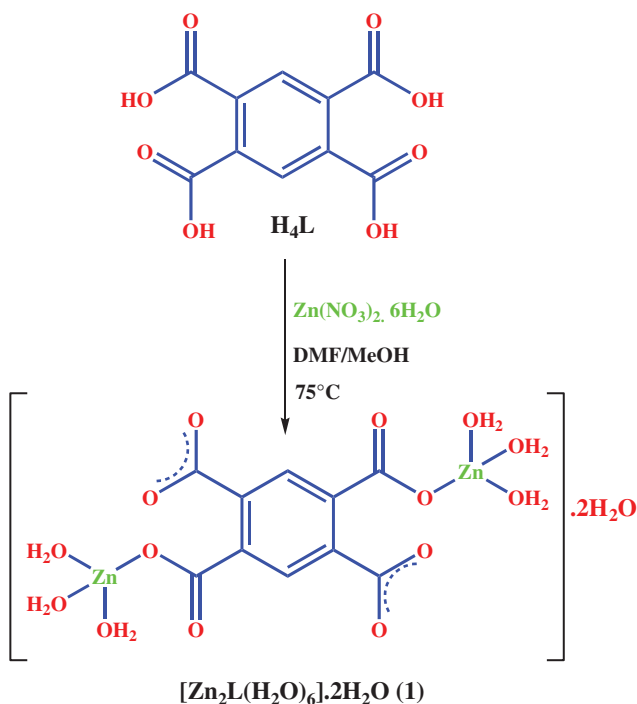
Hence, we reacted benzene-1,2,4,5-tetracarboxylic acid (H_4L) with Zn^{2+} salts and obtained the new (μ_2 -benzene-1,2,4,5-tetracarboxylato-O,O')-hexaaqua-dizinc(II)-dihydrate complex $[Zn_2L(H_2O)_6] \cdot 2H_2O$ (**1**) (H_4L = benzene-1,2,4,5-tetracarboxylic acid) (Scheme 1). Herein, we report the synthesis and crystal structure of this dinuclear Zn(II) complex obtained by single crystal X-ray diffraction analysis, and the compound was also subject to thermogravimetric and topological analyses.

Experimental

Materials and physical methods

All the reagents and solvents were purchased from commercial sources and used as received. Elemental (C, H and N) analyses were performed on a Perkin-Elmer 2400 II analyzer. IR spectra were recorded in the region 400–4000 cm^{-1} on a Perkin-Elmer RXIFT spectrometer with samples as KBr disks. Thermal properties were analyzed with a Perkin-Elmer system (STA6000) at a heating rate of 10 $^{\circ}C \text{ min}^{-1}$ under dinitrogen atmosphere. Powder X-ray diffraction (PXRD) was conducted in a D8 Advance Bruker AXS (Bragg Brentano geometry) theta-2theta diffractometer, with copper radiation (Cu $K\alpha$, $\lambda = 1.5406 \text{ \AA}$) and a secondary monochromator, operated at 40 kV and 40 mA. Flat plate configuration was used and the typical data collection range was between 5 $^{\circ}$ and 38 $^{\circ}$ (see Supporting Information, Figure S1).

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Scheme 1: Chemical diagram of the synthesis of **1** from H_4L .

Synthesis of $[\text{Zn}_2\text{L}(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$ (**1**)

The mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (74 mg, 0.25 mmol) and H_4L (25.4 mg, 0.1 mmol) was dissolved in 4 mL of DMF: MeOH (1:1 v/v) mixture. A white precipitate was obtained when the mixture was stirred at room temperature for 1 h. The precipitate was dissolved in 1 mL of 28% aqueous solution of NH_4OH , the resulting colorless solution was sealed in an 8 mL glass vessel and heated at 75 °C for 24 h. Subsequent gradual cooling to room temperature (0.2 °C min⁻¹) afforded block-like colorless crystals. Yield: 83% (based on Zn). Anal. Calcd. for $\text{C}_{10}\text{H}_{18}\text{O}_{16}\text{Zn}_2$ ($M = 525.00$): C, 22.88; H, 3.46; Found: C, 22.50; H, 3.06. FT-IR (KBr, cm⁻¹): 3440 (b), 3327 (bs), 1602 (s), 1584 (s), 1491 (m), 1419 (m), 1368 (s), 1313 (w), 1265 (m), 1248 (m), 1137 (w), 932 (m), 870 (w), 824 (w), 767 (w), 708 (m), 613 (w), 514 (w).

Crystal structure determination

Diffraction data were collected on a Bruker-APEX II SMART CCD diffractometer at 296 K. For data processing and absorption correction the packages SAINT [38] and SADABS [39] were used. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares based on F^2 using SHELXTL [40] and SHELXL-97 [41] packages. All the hydrogen atoms except those of water molecules were inserted at calculated positions with isotropic thermal parameters and refined. Water hydrogen atoms were located from difference Fourier map. Using anisotropic treatment for the non-hydrogen atoms and isotropic treatment for the hydrogen atoms, the final refinement converged at the R_1 value ($I > 2\sigma(I)$) 0.0410. The crystallographic data are summarized in Table 1. CCDC 1017891 contains the supplementary crystallographic data of **1** in this paper. These data

Tab. 1: Crystallographic data for $[\text{Zn}_2\text{L}(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$ (**1**).

Formula	$\text{C}_{10}\text{H}_{18}\text{O}_{16}\text{Zn}_2$
Formula weight	524.98
Crystal color	Colorless
Crystal system	Monoclinic
Space group	$C2/c$
$a/\text{Å}$	18.506(5)
$b/\text{Å}$	9.594(5)
$c/\text{Å}$	12.075(5)
$\beta/^\circ$	109.747(5)
$V/\text{Å}^3$	2018(2)
Z	4
T/K	296(2)
$2\theta/^\circ$	4.676–52.830
μ (Mo K α)/mm ⁻¹	2.451
$\rho_{\text{calcd}}/\text{g cm}^{-3}$	1.728
$F(000)$	1064
Absorption-correction	Multi-scan
Index ranges	$-23 < h < 23$ $-12 < k < 12$ $-15 < l < 15$
Reflections collected	20947
Independent reflections	2067
R_{int}	0.0246
$R_1^a/wR_2^b [I > 2\sigma(I)]$	0.0381/0.1082
R_1^a/wR_2^b [for all F_o^2]	0.0400/0.1110
GOF on F^2	1.111

can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

Results and discussion

Syntheses and characterization

The reaction of H_4L with zinc(II) nitrate hexahydrate under hydrothermal reaction condition in dimethylformamide, methanol and NH_4OH aqueous solution leads to the formation of $[\text{Zn}_2(\text{L})(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$ ($\text{L} = \text{benzene-1,2,4,5-tetracarboxylate}$) (**1**). At first, the reaction was carried out with the 2:1 ratio of metal to ligand, producing 74% yield but slight excess addition of the metal salt (metal:ligand = 2.5:1) generated much higher yield (83%).

In the IR spectra, the characteristic strong bands of coordinated carboxylate groups of **1** appear at 1584 cm⁻¹ for the asymmetric stretching and 1368 cm⁻¹ for the symmetric stretching. A strong absorption band at 1602 cm⁻¹ appeared due to the C–O stretching frequency of uncoordinated carboxylate groups. The O–H stretching frequency of water

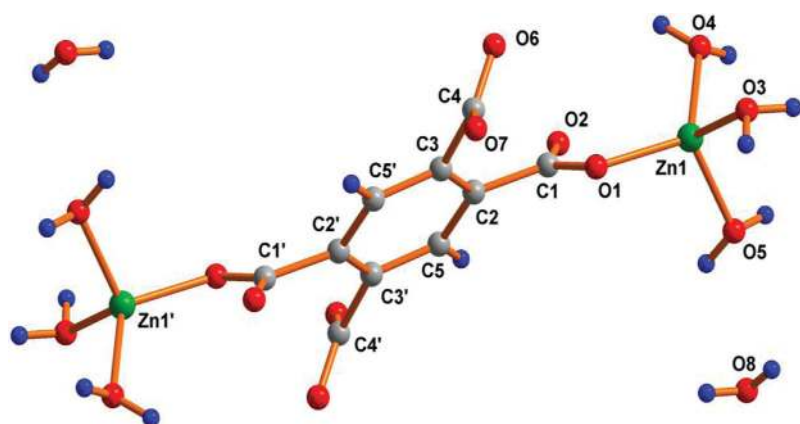


Fig. 1: Ball and stick presentation of the crystal structure of **1**. Symmetry: $1-x, -y, -z$.

molecules is visible at 3327 cm^{-1} . This compound was also characterized by single crystal X-ray diffraction (see below), powder X-ray diffraction (see supporting information) and elemental analysis (see Experimental section).

Crystal structure description

An idealized ball and stick presentation of the crystal structure of the $(\mu_2$ -benzene-1,2,4,5-tetracarboxylato- O,O')-hexaaqua-dizinc(II)-dihydrate complex $[\text{Zn}_2\text{L}(\text{H}_2\text{O})_6]\cdot 2\text{H}_2\text{O}$ (**1**) is depicted in Figure 1, while their selected bond lengths and angles are listed in Table 2. Crystal structure analysis shows that it is a dinuclear zinc(II) complex containing two Zn(II) centers μ_2 -bridged by a benzene-1,2,4,5-tetracarboxylate ligand (L^{4-}) while three water molecules are also connected to each metal center. Two solvated water molecules are also present in the crystal structure of **1**, which is symmetric due to the presence of an inversion center.

Similar to reported other polymeric Zn(II) compounds containing benzene-1,2,4,5-tetracarboxylic acid, the metal center (Zn1 or Zn1') in **1** adopts a tetrahedral coordination environment. As shown in Figure 1, one $\text{O}_{\text{carboxylate}}$ atom (O1) of a ligand (L^{4-}) and three O_{water} atoms (O3, O4 and O5) defines the tetrahedral coordination environment for the zinc(II) center.

Tab. 2: Selected bond lengths (Å) and angles ($^\circ$) for $[\text{Zn}_2\text{L}(\text{H}_2\text{O})_6]\cdot 2\text{H}_2\text{O}$ (**1**). Symmetry as in the Figure 1.

Zn1–O1	1.989(2)	O1–Zn1–O3	101.4(1)
Zn1–O3	2.025(3)	O1–Zn1–O4	121.4(1)
Zn1–O4	2.018(3)	O1–Zn1–O5	110.3(1)
Zn1–O5	2.018(3)	O3–Zn1–O4	107.7(1)
		O3–Zn1–O5	110.4(1)
		O4–Zn1–O5	105.4(1)

The $\text{Zn}-\text{O}_{\text{water}}$ bond distances (2.018(3)–2.025(3) Å, Table 2) are slightly longer than the $\text{Zn}-\text{O}_{\text{carboxylate}}$ bond distance (1.989(2) Å) while the $\text{O}_{\text{water}}-\text{Zn}-\text{O}_{\text{carboxylate}}$ or $\text{O}_{\text{water}}-\text{Zn}-\text{O}_{\text{water}}$ bond angles are in the range of $101.37(9)$ – $121.42(10)^\circ$, which indicates that the tetrahedral coordination environment is highly distorted.

As shown in Figure 2, the crystal lattice of the compound contains a number of non-covalent H-bonding interactions involving the coordinated (O3, O4 and O5) and solvated (O8) water molecules and coordinated (O1) and non-coordinated (O2, O6 and O7) carboxylate oxygen atoms. Interactions between these water molecules (coordinated or solvated) and carboxylate moieties (coordinated or free) stabilized an overall three dimensional supramolecular associate (Figure 3).

All the three coordinated water molecules (O3, O4 and O5) act as strong or moderate H-donors [$d(\text{D}\cdots\text{A}) = 2.952$ – 3.205 Å and $\angle\text{D}-\text{H}\cdots\text{A} = 140$ – 176° , Table 3] to the coordinated (O1) and non-coordinated (O2 and O6) carboxylate oxygens and to the solvated water molecule (O8) while the solvated water (O8) acts not only as acceptors (to the coordinated water molecules, O3) but also as donors (to the non-coordinated carboxylate oxygens, O6 and O7) to vicinal molecules. Interactions formed by this solvated water molecules are also of different strength as evidenced by the geometric parameters [$d(\text{D}\cdots\text{A}) = 2.713$ – 3.091 Å and $\angle\text{D}-\text{H}\cdots\text{A} = 132$ – 167° , Table 3].

Topological analyses

Topological analysis [42] of the hydrogen bonded network of **1** has been carried out. The 3D hydrogen bonded network (Figure 4) in **1** can be represented as a 3, 16-connected binodal net and the point symbol for this net is

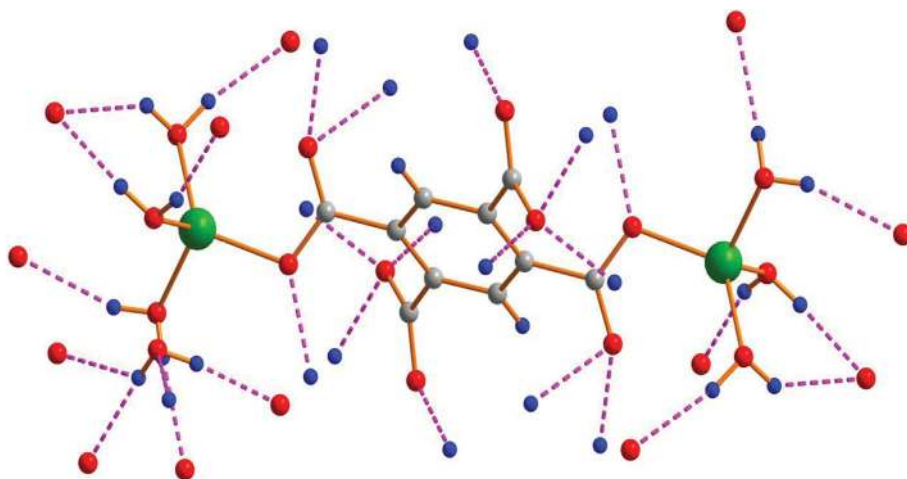


Fig. 2: Ball and stick presentation of the hydrogen bonding interactions in **1**. Color code: hydrogens, blue; oxygens, red; carbons, ash and zinc, green.

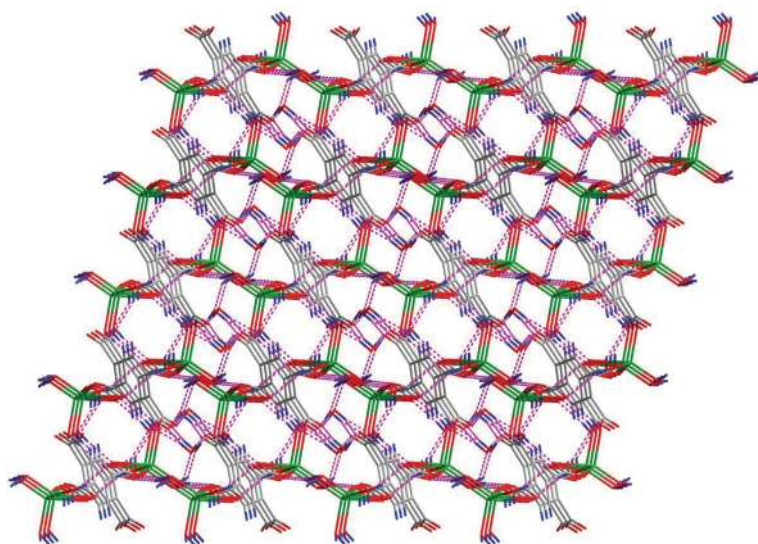


Fig. 3: Idealized wire and stick presentation of the hydrogen bonded 3D network in the crystal lattice of **1**.

Tab. 3: Geometries [distances in (Å) and angles in (°)] of the H-bonds in $[\text{Zn}_2\text{L}(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$ (**1**). Symmetry: *i*) $0.5-x, 0.5-y, -z$; *ii*) $0.5-x, 0.5+y, 0.5-z$; *iii*) $x, 1-y, 0.5+z$; *iv*) $1-x, 1-y, -z$; *v*) $1-x, y, 0.5-z$; *vi*) $x, -y, 0.5+z$.

D-H...A	D...A	H...A	D-H...A
O3-H3A...O1 ⁱ	3.066(4)	2.197(2)	176(4)
O3-H3B...O8 ⁱⁱ	3.091(4)	2.25(3)	156(5)
O4-H4A...O6 ⁱⁱⁱ	3.062(4)	2.32(3)	140(3)
O4-H4B...O2 ^{iv}	3.205(4)	2.34(2)	159(3)
O5-H5A...O6 ⁱⁱⁱ	2.990(4)	2.16(2)	155(4)
O5-H5B...O2 ^v	2.952(3)	2.08(2)	162(4)
O8-H8A...O6 ⁱ	2.934(4)	2.10(2)	167(4)
O8-H8A...O7 ⁱ	3.068(4)	2.44(3)	132(3)
O8-H8B...O7 ^{vi}	2.713(3)	1.90(2)	164(4)

$\{3^2.4\}_2\{3^{20}.4^{40}.5^{38}.6^{17}.7^5\}$. In compound **1**, the binuclear zinc complex unit being hydrogen bonded with 16 different entities, represents a 16-connected node, whereas remaining the water molecule are hydrogen bonded with 3 different units acts as a 3-connected node.

Thermal property

Thermogravimetric measurements were carried out under dinitrogen atmosphere in the range from room temperature to ca. 750 °C at a heating rate of 10 °C min⁻¹. Features of the thermal stability of complex **1** are illustrated in Figure 5.

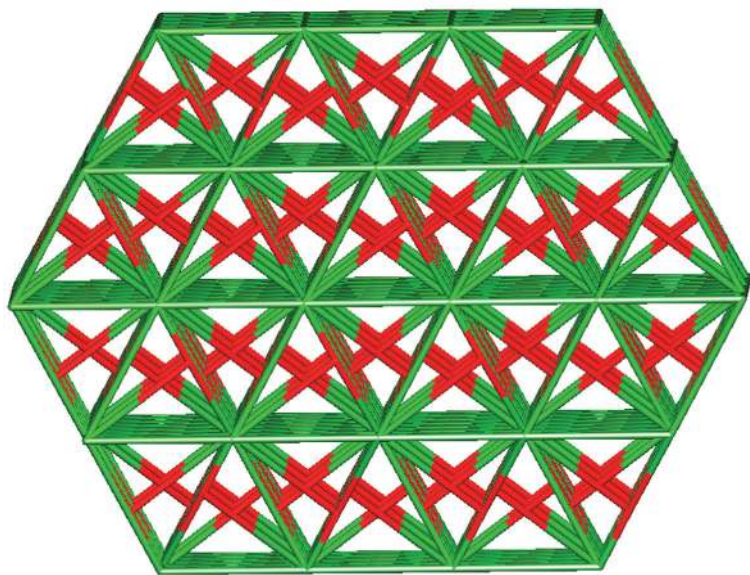


Fig. 4: Node-and-linker-type descriptions of the 3D hydrogen bonded framework of 1.

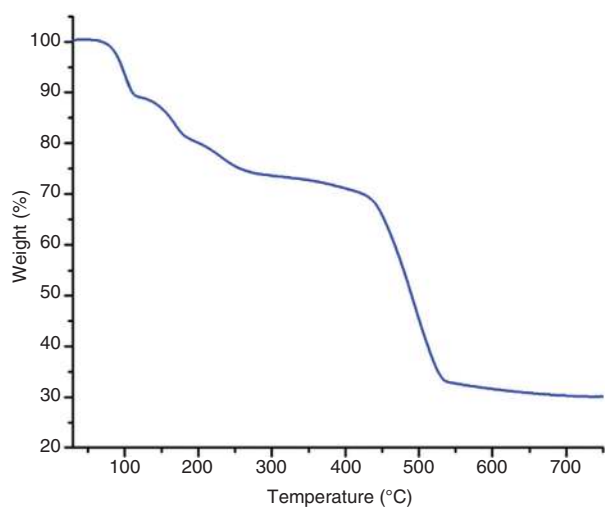


Fig. 5: Thermogravimetric curve for 1.

Complex 1 shows a weight loss of 26.9% between 55 and 334 °C, corresponding to the loss of eight water molecules (calcd: 27.4%). The remaining material is stable up to 405 °C, and beyond which it decomposes until 554 °C.

Conclusion

We have synthesized the new (μ_2 -benzene-1,2,4,5-tetracarboxylato-O,O')-hexaaqua-dizinc(II)-dihydrate complex $[\text{Zn}_2\text{L}(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$ (1) by reacting benzene-1,2,4,5-tetracarboxylic acid (H_4L) with Zn(II) salt in DMF/MeOH.

Despite the availabilities of four carboxylates of the ligand (L^{4-}), only two coordinate to the Zn(II) center to stabilize a dinuclear complex. Although plenty of polymeric zinc(II) compounds containing benzene-1,2,4,5-tetracarboxylate have been reported, a dimeric zinc(II) complex is not known. To our knowledge, it is the only dinuclear zinc(II) complex containing benzene-1,2,4,5-tetracarboxylate. Topological analysis of the 3D H-bonded network has been also carried out. Synthesis and study of the similar type of compounds are in progress.

Acknowledgments: Financial supports from the Fundação para a Ciência e a Tecnologia (FCT), Portugal for fellowship grants (Ref. Nos. SFRH/BPD/78264/2011 and SFRH/BPD/76192/2011) and the Council for Scientific and Industrial Research (CSIR), Government of India to S. Hazra and A. Karmakar are gratefully acknowledged.

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Supplemental Material: The online version of this article (DOI: 10.1515/zkri-2014-1812) offers supplementary material, available to authorized users.